



Enhanced electricity generation for microbial fuel cell by using electrochemical oxidation to modify carbon cloth anode



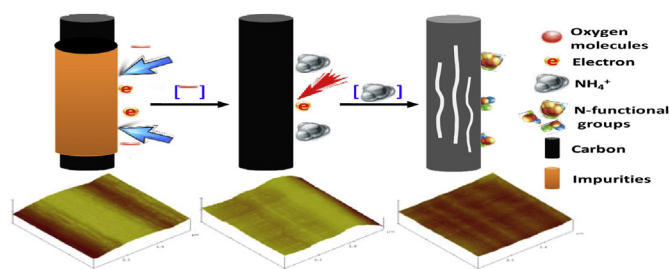
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HIGHLIGHTS

- A convenient electrochemical oxidation method for anodic modification of MFC.
- EASA and exchange current density were enhanced by 2.9 times and 41%.
- Amide and nitrogen functional groups were introduced by the anode modification.
- Electron transfer efficiency and power output were dramatically enhanced.

GRAPHICAL ABSTRACT



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ABSTRACT

Different types of treatment methods for anode materials are reported to enhance power production in microbial fuel cells (MFCs). Here we report a simple, cost-effective and environmentally friendly electrochemical oxidation technique that is used to modify the carbon cloth for the improvement of MFC performance. Carbon cloth is immersed in a 5% NH_4HCO_3 solution and then the solution is oxidized at different set currents. Optimal performance is obtained at 14 mA cm^{-2} with an oxidation time of 2 min, based on production of a maximum power density of $939 \pm 7 \text{ mW m}^{-2}$ in MFC tests, which is 14.2% higher than that of the untreated carbon cloth control. This treatment method increases the electrochemical active surface area by 2.9 times (from 11.2 to 44.1 cm^2), and improves the exchange current density by 41% (from 4.79×10^{-4} to $6.76 \times 10^{-4} \text{ A m}^{-2}$). XPS analysis indicates that electrochemical oxidation in this solution introduced amide groups onto the electrode surface, which likely improves bacterial adsorption and current production. These results show that simple electrochemical treatment method can increase active surface area and alter carbon cloth anodes in ways that increase power production of the MFC.

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1. Introduction

Microbial fuel cells (MFCs) are technologies that use exoelectrogenic bacterial to directly transform chemical energy to electrical energy, while degrading organic pollutants in wastewater [1,2]. MFCs have drawn attention as a novel method for wastewater

treatment, generation of renewable energy resources, and environmental bioremediation [3–5]. The energy stored in organic matter is released during exoelectrogenic bacterial metabolism as electrical current to the anode surface [6]. Thus, improving anode performance is important for increasing power production using MFCs [7].

The anodes used in MFCs can be improved by increasing specific surface area, electrical conductivity, electrochemical stability, and biocompatibility, while reducing electrode costs [8]. The most widely used MFC anode materials are made from carbon materials,

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including carbon paper, carbon cloth, carbon felt, carbon fiber brush, graphite rods, and graphite plates [9]. Previous research has shown that electrode performance can be improved through chemical modifications of the anode. N-functional group doped treatments have significantly increased the maximum power density. Cheng et al. showed that ammonia gas treatment (700 °C for 1 h) improved the maximum power density of an MFC by 20%, compared to the untreated carbon cloth [10]. Feng et al. used a simpler heat treatment (450 °C for 30 min) without ammonia that increased the maximum power output of an MFC with carbon fiber brush anodes by 25%. This result showed that the process improved performance due to the increase in the N1s/C1s ratio [11]. Zhu et al. modified the carbon fiber felt by applying nitric acid and ethylenediamine, which reduced the start-up time by 45% and 51% compared to unmodified anode materials [12]. The observed differences were attributed to variations in functional groups on the anode surface. Adding anthraquinone disulfonate (AQDS) into a polypyrrole (PPy) membrane to modify the carbon felt anode was also shown to improve power production of the MFC due to the increase of the electron transfer efficiency and bacteria attached to the anode [13]. Using pyrrole, a nontoxic macromolecule polymer to modify carbon cloth anode, the initial power density increased from 20 mW m⁻² to 160 mW m⁻² [14]. Qiao et al. examined the electrocatalytic activity of polyaniline-coated electrode and a carbon nanotube/polyaniline electrode on nickel foam. They found that the polyaniline/carbon nanotube electrode had better performance than the polyaniline electrode [15]. Although heat treatment methods or chemical modification techniques can enhance the performance of MFCs, special demands are required during the treatment process, including specific complicated apparatus, high treatment temperatures, long treatment time or expensive chemicals. So that the capital costs may be increased and the application of these techniques will be blocked.

Electrochemical oxidation technology has been regarded as a simple, efficient, cost-effective and environmentally friendly electrochemical processing technique for material surface modification [16]. Compared with other electrode modification techniques, the electrochemical oxidation method can be used to clean the electrode surface, remove the impurities on the surface, improve the mechanical strength of the carbon material [17,18] and increase the adhesion of bacteria to the surface [19]. Ammonium bicarbonate (NH₄HCO₃) is comparatively mild electrolyte solution that can be used to decrease oxygen functional groups on the surface of materials [20]. Previous results showed that the decrease in the relative content of oxygen functional groups on the surface of treated anodes could improve power output of MFC [7,11]. Therefore, we examined the use of electrochemical oxidation treatment of carbon anodes in a NH₄HCO₃ solution as a method to enhance the electrochemical activity of the carbon cloth electrode. The characteristics of the anode surface, the changes of the surface function groups, and the performance of the MFCs with these electrochemically treated electrodes were compared before and after the treatment under different oxidation current densities.

2. Materials and methods

2.1. Electrochemical oxidation treatment of anodes

All anodes were made of non-wet proofed carbon cloth (E-TEK, USA) that were soaked in acetone overnight, and then rinsed in ultrapure water (18.2 MΩ cm at 25 °C) before use. Electrochemical oxidation of the carbon electrodes was carried out using an electrochemical workstation (CHI600D, CH Instruments Inc., China). A two-electrode system was used with carbon cloth (CC) as the working electrode, stainless steel electrode as the counter electrode,

and a 2 cm inter-electrode spacing. NH₄HCO₃ (5%) was used as the electrolyte. Current densities were set to 0, 3, 7 and 14 mA cm⁻², and reaction time was 2 min for the electrochemical oxidation. Treated carbon cloth electrodes were then rinsed with ultrapure water five times to remove the residual chemicals, and dried in an oven at 105 °C for 2 h before use.

2.2. MFC construction and operation

Single chambered, cubic-shaped reactors were used with an anode chamber 2 cm in length by 3 cm in diameter (liquid volume of 14 mL, projected surface area of the cathode of 7 cm²) [21]. Air cathodes were made of carbon cloth (type B-1B, 30% wet proofing, E-TEK, USA) with 0.35 mg cm⁻² Pt/C catalyst (C1-10 10% HP Pt on Vulcan XC-72, BASF, USA) on the water side using a Nafion (5 wt%, Sigma-Aldrich, USA) binder, four polytetrafluoroethylene (PTFE) diffusion layers on the air side (Dupont, USA) as previously described [22]. All MFCs were inoculated with domestic wastewater (30%, v/v) from the Wenchang Wastewater Treatment Plant, and operated in fed-batch mode at a fixed external resistance of 1000 Ω (unless otherwise specified). The MFCs were fed sodium acetate as the substrate (1 g L⁻¹) in a 50 mmol L⁻¹ phosphate buffer solution (PBS, pH 7.0) containing mineral (12.5 mL L⁻¹) and vitamin (5 mL L⁻¹) solutions [23]. Tests were conducted using duplicate reactors at 30 °C in a temperature-controlled room.

2.3. Chemical and electrochemical analysis

Multi-modal imaging Atomic Force Microscopy (AFM, Veeco Instruments Inc, USA) was performed at room temperature and a relative humidity of 30%. The images of the carbon fiber surface before and after modification were analyzed and processed using the Nanoscope III software supplied by the AFM. Both characterization of surface composition and functional group distribution of the carbon fiber surfaces were measured by X-ray photoelectron spectroscopy (XPS; PHI 5700 ESCA System, Physical Electronics, USA) with a monochromatic Al Kα X-ray radiation source (hν = 1486.6 eV) at an incident angle of 90° [11]. The bulk element composition of sample was obtained over a scan range of 1350–0 eV. All electron binding energies were referenced to the C1s spectrum of neutral graphitic carbon peak at 284.6 eV. The XPS spectra data was accomplished with the software MultiPak V6.1A (Physical Electronics Inc.).

Electrochemical active surface area (EASA) tests were conducted using MFC reactors containing a working electrode (modified or plain carbon cloth anodes), a counter electrode (Pt plate), and an Ag/AgCl reference electrode (195 mV vs. SHE, Spisc-Rex Instrument Factory, China). The electrolytes contained 5 mM K₄Fe(CN)₆ and 0.2 M Na₂SO₄. EASA tests were estimated by cyclic voltammetry (CV) over the scan range of −0.4 V to +1.0 V [7]. Exchange current density (*i*₀, A cm⁻²) measurements were performed at the open circuit potentials of the anode (vs. Ag/AgCl reference electrode) with a sweep rate of 1 mV s⁻¹ over the over potential range (*η*) of 0 mV–100 mV [24]. Both the electrochemical active surface area and exchange current density measurements were tested using an electrochemical workstation (model 263A, AMETEK-AMT, US). The electrochemical active surface area (EASA) was calculated by Butler–Volmer equation as previously described [7]. Both exchange current density (*i*₀, A m⁻²) and kinetic activity (KA) were calculated by Tafel plots as previously described [24].

2.4. Calculations

Cell voltages (*U*, V) across the external resistor (1000 Ω, except as noted) were measured at a time interval of 30 min using a data

acquisition system (PISO-813, ICP DAS Co., Ltd.). Current density ($i = U/AR_{\text{ex}}$) (i , A m^{-2}) and power density ($P = U^2/AR_{\text{ex}}$) (P , mW m^{-2}) were calculated as previously described, where U (V) is the voltage when MFCs reached a steady-state condition, R_{ex} (Ω) is the external resistor, A (m^2) is the cross sectional area of the cathode [25]. The polarization curves and power density curves were obtained by the single-cycle method using a series of external circuit resistances varied from the open circuit voltage (OCV) to 50Ω in decreasing order (30 min per resistance) [26].

3. Results and discussion

3.1. MFC performance

The maximum power density of MFC was significantly improved by the anode performance treated with different current densities (Fig. 1A, B). The maximum power density of $939 \pm 7 \text{ mW m}^{-2}$ was obtained at the oxidation current density of 14 mA cm^{-2} (CC-14), which was 14.2% higher than that of MFCs using untreated carbon cloth (CC). This was 4% higher than that obtained at 7 mA cm^{-2} (CC-7, $903 \pm 9 \text{ mW m}^{-2}$) and 7% higher compared to 3 mA cm^{-2} (CC-3, $880 \pm 10 \text{ mW m}^{-2}$). The lowest power density of $822 \pm 8 \text{ mW m}^{-2}$ was produced by untreated carbon cloth. The measured electrode potentials showed that the anode potential was responsible for the differences in power densities, while the cathodes showed similar potentials at the different current densities (Fig. 1C). The anode potentials were gradually decreased (more negative) with the increase in current density. Previous results showed that the relative negative anode potential can indicate the better activity of anode communities [27]. Thus, the more negative anode potential probably due to facilitated the growth, adhesion and activity of bacteria.

3.2. Anode surface morphology and roughness analysis

AFM three-dimensional images of the electrode surface structures showed differences in morphologies before and after the electrochemical oxidation treatments (Fig. 2). The surfaces of the plain carbon cloth fibers showed a clear fibrous skeleton, a uniform surface structure, and it had a relatively smooth surface along the fiber length (Fig. 2A). Protrusions were found on the surface of plain carbon cloth, showing some impurities on the surface. In contrast, the surface of the carbon after electrochemical treatment lacked these impurities (Fig. 2B–D), which indicated that the electrochemical oxidation treatment had a cleaning effect. The etching mark on the electrode surface was observed. The etching degree enhanced with the increasing of oxidation current densities. As shown in Fig. 2B, a slight striation structure was produced on the surface using the 3 mA cm^{-2} treatment. With the treatment at 7 mA cm^{-2} , these striations deepened and more grooves were produced (Fig. 2C). After oxidation treatment at 14 mA cm^{-2} , a part of the skeleton on the fiber surface was etched, and the new surfaces and edges appeared smooth (Fig. 2D).

The surface roughness of both plain and treated electrode material was evaluated in terms of the arithmetic mean of the absolute values of the surface height deviations relative the center line, R_a . The surface roughness of the plain carbon cloth ($R_a = 12 \text{ nm}$) was increased from 31 nm at 3 mA cm^{-2} to 49 nm at 7 mA cm^{-2} . When the current density was further increased to CC-14, R_a decreased to 23 nm due to the increase of current shear force. The surface roughness findings are consistent with the evidence of AFM three-dimensional images of the electrodes. The relatively higher surface roughness compared with untreated plain carbon cloth could conducive to improve the three-dimensionally interface with electrode and facilitate bacterial adhesion on the electrode surfaces [28,29]. The power density of MFC was increased with the increase

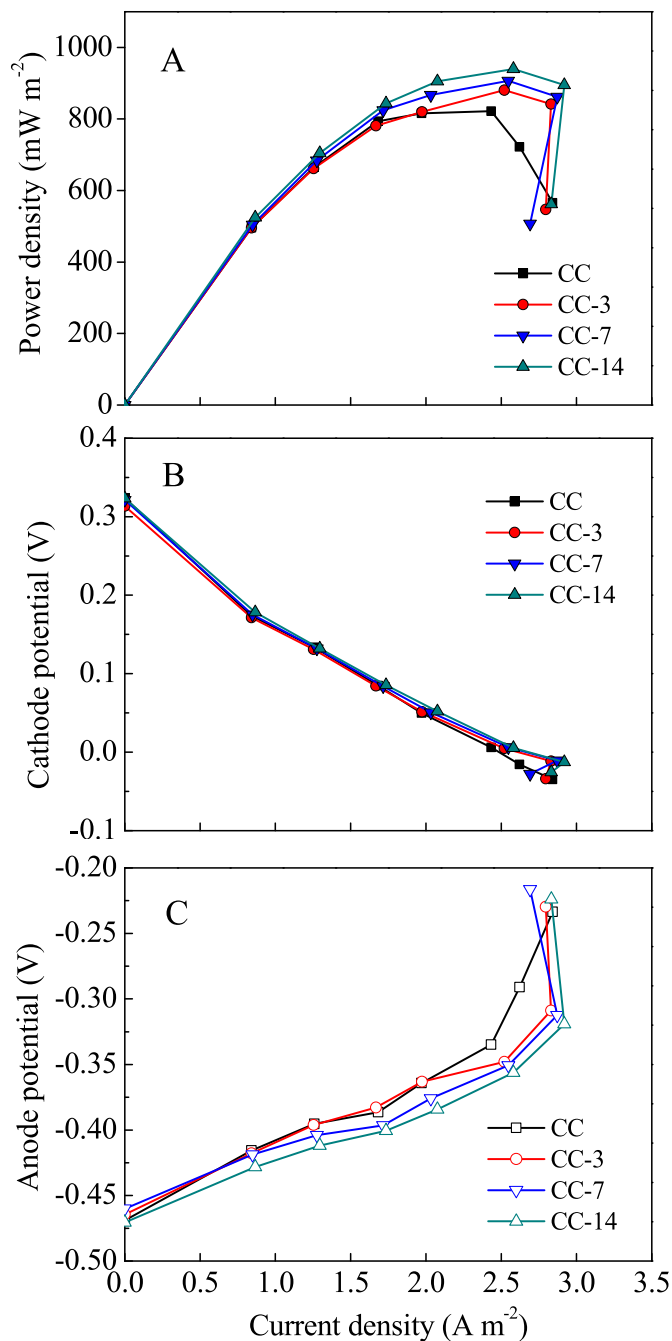


Fig. 1. (A) Polarization curves, (B) cathode potentials, and (C) anode potentials curves (vs. Ag/AgCl electrodes) using different current density. CC: untreated carbon cloth, CC-3: 3 mA cm^{-2} , CC-7: 7 mA cm^{-2} , CC-14: 14 mA cm^{-2} .

of surface roughness. The maximum power density was achieved by using CC-14, despite the reduction in the surface roughness of CC-14, which was probably due to new surfaces or some functional groups appeared on the electrode interface and promoted the bacteria adhesion to the anode.

3.3. Surface characteristics of anode

To further evaluate both electronic structure and chemical characteristics of untreated and treated anode, the electrodes were examined using XPS. The XPS results indicated the presence of C ($\text{BE} \approx 284.5 \text{ eV}$) and O ($\text{BE} \approx 531.5 \text{ eV}$) elements on the surface of

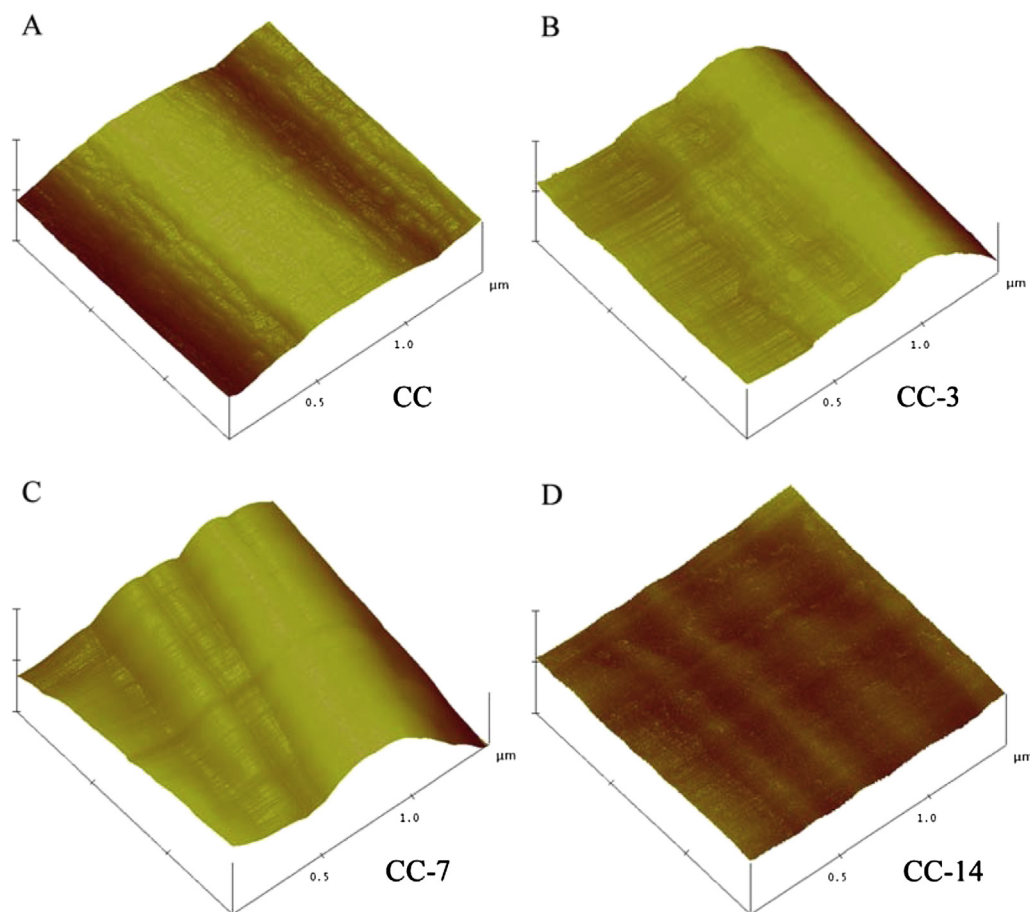


Fig. 2. AFM photographs of untreated carbon cloth (A) and after electrochemical oxidation treatment (B–D) using different current density. CC: untreated carbon cloth, CC-3: 3 mA cm^{-2} , CC-7: 7 mA cm^{-2} , CC-14: 14 mA cm^{-2} .

plain carbon cloth (Fig. S1). After the electrochemical oxidation treatment, extra elements N ($\text{BE} \approx 400 \text{ eV}$) were found on the surfaces of the cloth treated at 14 mA cm^{-2} (Table S1), and the relative elemental amounts of O1s decreased from 9.96% to 6.6%. The relative elemental amounts of O1s decrease might be a result of the cleaning of the electrode surface by electrochemical oxidation treatment, and also the N introduced on the surface would have decreased the relative O content [7]. The N/C ratio increased from 0 (control, CC) to 0.80% (CC-3), 1.26% (CC-7) and 1.14% (CC-14), and the O/C ratio decreased after electrochemical oxidation treatment.

New hydrophilic functional groups were introduced through the interaction of the electrode and electrolyte. After the electrochemical oxidation treatment, the N1s peak distribution was consisted of distinctive bonds which had different binding energies (Fig. 3) and different surface functional groups, such as C–N, $\text{O}=\text{C}-\text{NH}_2$, $\text{N}=\text{O}$ and $\text{O}-\text{N}-\text{O}$ (Fig. 4). Amide groups were found and their content increased with oxidation current density. The highest value 52.7% was produced using CC-14. The increase in amide group concentration was likely due to the ionized ammonium ions contacting to electrode surface, where they reacted with carboxylic acid functional groups on the surface of the carbon material to form the N-functional group. The trend in the relative abundance of amide group based on XPS analysis showed a positive correlation with maximum power densities, which was attributed to the increased nitrogen-containing functional groups after electrochemical oxidation. In addition, the surface charge transfer and hydrophilicity were also changed, which could have improved bacterial adhesion on the electrode surface and resulted in higher power

output of the MFCs. Previous results using a different approach showed that an increase of amino groups on the material surface could improve the electron transfer from microorganism to the surface of the electrode [10]. The nitrogen ion implantation on the carbon paper electrode can also increase the conductivity, water contact angle and biofilm attachment between the bacteria and the electrode [29]. When the anode surface was chemically modified, the addition of nitrogen-containing functional groups such as C–N, $\text{C}=\text{N}$ might promote the improved performance of the electrode [30]. Furthermore, the amide group could increase the adsorption of bacteria to the electrode surface [31]. Consequently, the improved results with electrochemical oxidation treatment might be explained by the modification of electrode surface coupled to the emergence of nitrogen-containing functional groups.

3.4. Electrochemical analysis of modified anodes

The electrochemical performance of both untreated and treated electrode materials was evaluated by both cyclic voltammetry (CV) and changes in electrochemical active areas (Fig. 5). The relative potential changes of redox peaks observed using different modified electrodes might be ascribed to the different charge transfer coefficient [7] and electrostatic force [32], which indicated that the different functional groups were successfully introduced to the electrode surfaces by the electrochemical oxidation. The peak current, the surface area of electrochemical activity, and the charge transfer coefficient all improved with higher oxidation current densities. The peak current of the plain carbon had the lowest

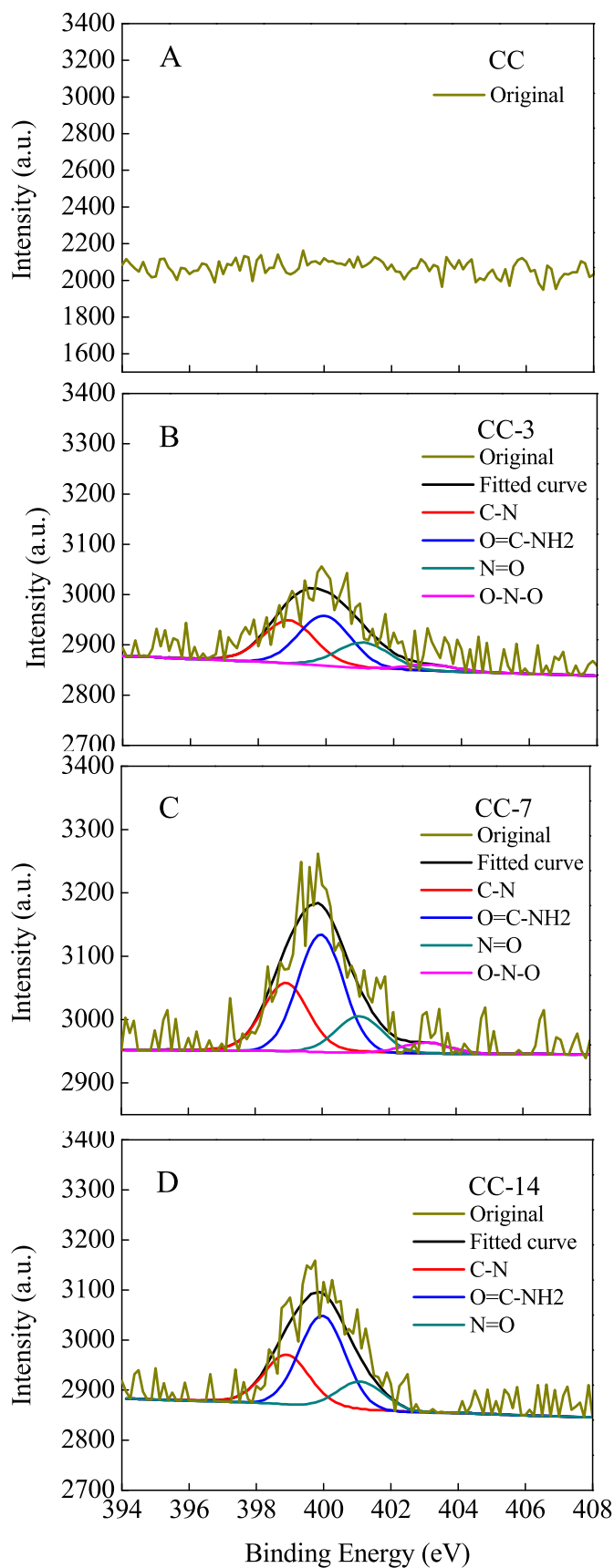


Fig. 3. High-resolution N1s spectra of the untreated (A) and electrochemical oxidation treatment (B to D). (A) CC: untreated carbon cloth; (B) CC-3: 3 mA cm^{-2} ; (C) CC-7: 7 mA cm^{-2} ; (D) CC-14: 14 mA cm^{-2} .

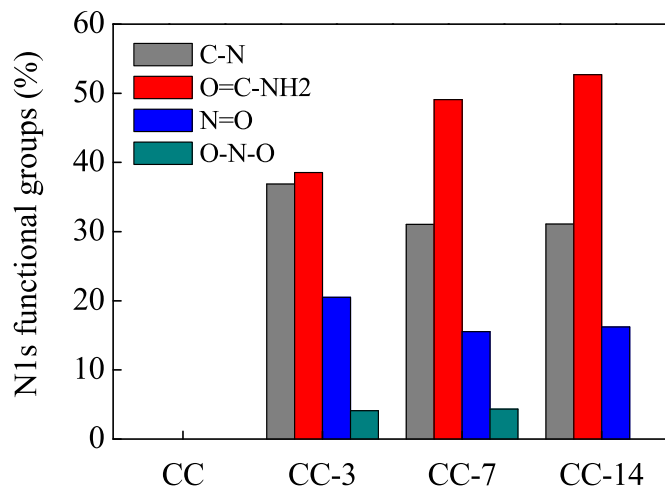


Fig. 4. The different surface functional groups percentages of N 1s spectra. CC: untreated carbon cloth, CC-3: 3 mA cm^{-2} , CC-7: 7 mA cm^{-2} , CC-14: 14 mA cm^{-2} .

current response of 8.0 mA in the CV tests, indicating that electrode surface without treatment had a little activity toward electron transfer. The peak current of CC-14 significantly increased to 31.6 mA , which was three times higher than that of the untreated (control) anode. The electrochemical activity area and the charge transfer coefficient (β) of CC-14 were 2.9 times (from 11.2 to 44.1 cm^2) and 2.8 times (from 0.15 to 0.57) higher than of the untreated control electrode (Table 1). Increases in surface charge and charge transfer coefficients are consistent with improved electrode performance [7].

3.5. The kinetic characteristics of the anodes

The exchange current density (j_0) depends on the linear area of the Tafel curve, and it is the main factor used to evaluate the charge transfer coefficient of an electrode. A linear Tafel regression existed ($R^2 > 0.99$) in the over potential interval of 60 and 100 mV (Fig. 6). The open circuit potential, j_0 and kinetic activity (KA) of anodic reaction were given in Table 2. The open circuit potential for electrodes treated at increased oxidation current densities became

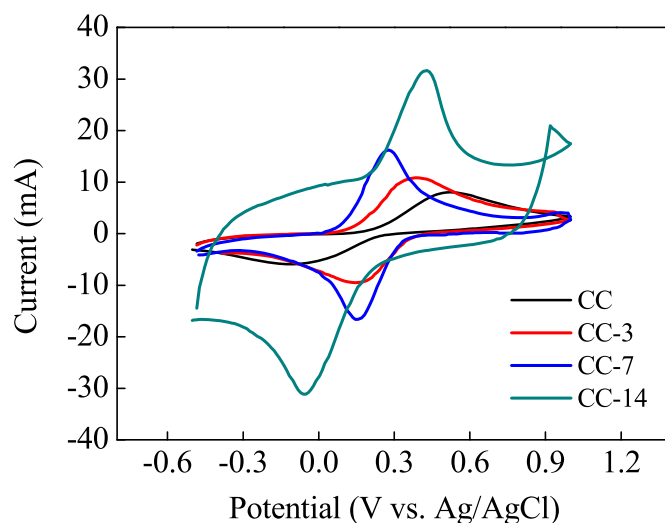


Fig. 5. Cyclic voltammetry (CV) of carbon cloth before and after electrochemical oxidation treatment using different current density in $5 \text{ mM K}_4\text{Fe}(\text{CN})_6$ system. CC: untreated carbon cloth, CC-3: 3 mA cm^{-2} , CC-7: 7 mA cm^{-2} , CC-14: 14 mA cm^{-2} .

Table 1

Transfer coefficients and electrochemical active area of untreated and electrochemical oxidation treatment with different oxidation current.

	i_p (mA)	A (cm ²)	Slope	β
CC	8.03	11.20	2.48	0.15
CC-3	9.09	12.68	4.46	0.27
CC-7	15.54	21.67	5.18	0.31
CC-14	31.62	44.11	9.26	0.57

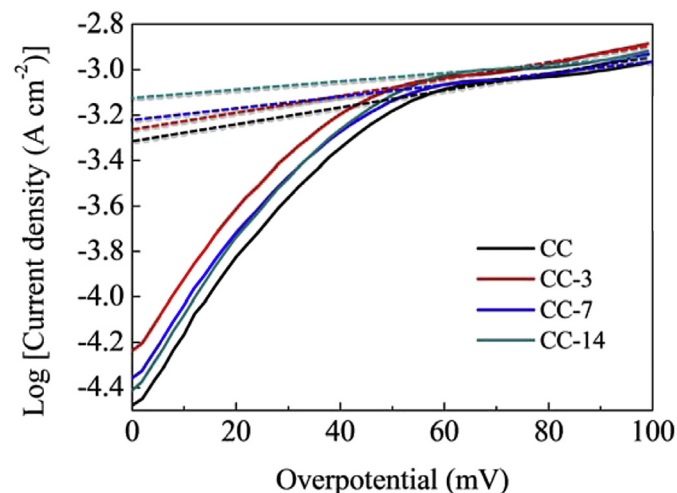


Fig. 6. Tafel plots of MFC with carbon cloth electrodes before and after electrochemical oxidation treatment. The scan rate is 1 mV s⁻¹, from $\eta = 0$ –100 mV, where $\eta = 0$ is the open circuit potential.

more negative compared to the control, indicating that electrochemical oxidation improved the electrode performance. This result was consistent with that obtained with CV and polarization curve analyses. The j_0 and KA were increased with oxidation current density. The CC-14 had the highest KA, which was 41% higher than that obtained with the untreated CC, and the j_0 values was increased from 4.79 (CC) to 6.76 A cm⁻² (CC-14). The increase of both j_0 and KA may be attributed to the changed surface structure and facilitated electron transfer. Thus, it was clearly shown that the rate of the electron transfer of the anode could be improved by electrochemical oxidation.

4. Conclusions

An optimal operating condition for electrochemical oxidation was obtained of 14 mA cm⁻² at 2 min, with an increase in the power density of 14.2%. The exchange current density i_0 was also increased by 41% compared to the untreated control. The electrochemical oxidation greatly changed the electrode surface structure and introduced amide groups and nitrogen functional groups to the surface, which enhanced electrochemical performance. Electrochemical oxidation improved the electrochemical activity of the electrode, increased the bioaccessible surface area and facilitated

electron transfer. Therefore, these results showed that electrochemical oxidation of the anode was an effective method for modification to improve MFC performance.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.04.005>.

References

- [1] B.E. Logan, B. Hamelers, R.A. Rozendal, U. Schröder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete, K. Rabaey, *Environ. Sci. Technol.* 40 (2006) 5181–5192.
- [2] R.A. Rozendal, H.V.M. Hamelers, K. Rabaey, J. Keller, C.J.N. Buisman, *Trends Biotechnol.* 26 (2008) 450–459.
- [3] J. Liu, Y.J. Feng, W.H. He, Y.Y. Gong, Y.P. Qu, N.Q. Ren, *J. Power Sources* 248 (2014) 317–322.
- [4] Y.P. Qu, Y.J. Feng, J. Liu, W.H. He, X.X. Shi, Q. Yang, J.W. Lv, B.E. Logan, *Desalination* 317 (2013) 17–22.
- [5] D.R. Lovley, *Energy Environ. Sci.* 4 (2011) 4896–4906.
- [6] H.V.M. Hamelers, A. Ter Heijne, T.H.J.A. Sleutels, A.W. Jeremiasse, D.P.B.T.B. Strik, C.J.N. Buisman, *Appl. Microbiol. Biotechnol.* 85 (2010) 1673–1685.
- [7] X. Wang, S.A. Cheng, Y.J. Feng, M.D. Merrill, T. Saito, B.E. Logan, *Environ. Sci. Technol.* 43 (2009) 6870–6874.
- [8] B.E. Logan, *Appl. Microbiol. Biotechnol.* 85 (2010) 1665–1671.
- [9] J.C. Wei, P. Liang, X. Huang, *Bioresour. Technol.* 102 (2011) 9335–9344.
- [10] S.A. Cheng, B.E. Logan, *Electrochem. Commun.* 9 (2007) 492–496.
- [11] Y.J. Feng, Q. Yang, X. Wang, B.E. Logan, *J. Power Sources* 195 (2010) 1841–1844.
- [12] N.W. Zhu, X. Chen, T. Zhang, P.X. Wu, P. Li, J.H. Wu, *Bioresour. Technol.* 102 (2011) 422–426.
- [13] C.H. Feng, L. Ma, F.B. Li, H.J. Mai, X.M. Lang, S.S. Fan, *Biosens. Bioelectron.* 25 (2010) 1516–1520.
- [14] D.Q. Jiang, B.K. Li, *Water Sci. Technol.* 59 (2009) 557–563.
- [15] Y. Qiao, C.M. Li, S.J. Bao, Q.L. Bao, *J. Power Sources* 170 (2007) 79–84.
- [16] C.M. Yoon, D.H. Long, S.M. Jang, W.M. Qiao, L.C. Ling, J. Miyawaki, C.K. Rhee, I. Mochida, S.H. Yoon, *Carbon* 49 (2011) 96–105.
- [17] A. Fukunaga, S. Ueda, *Compos. Sci. Technol.* 60 (2000) 249–254.
- [18] M.H. Zhou, M.L. Chi, H.Y. Wang, T. Jin, *Biochem. Eng. J.* 60 (2012) 151–155.
- [19] X.H. Tang, K. Guo, H.R. Li, Z.W. Du, J.L. Tian, *Bioresour. Technol.* 102 (2011) 3558–3560.
- [20] Y.J. Ma, J.L. Wang, X.P. Cai, *Int. J. Electrochem. Sci.* 8 (2013) 2806–2815.
- [21] X. Wang, Y.J. Feng, J. Liu, X.X. Shi, H. Lee, N. Li, N.Q. Ren, *Biosens. Bioelectron.* 26 (2010) 946–948.
- [22] J. Liu, Y.J. Feng, X. Wang, Q. Yang, X.X. Shi, Y.P. Qu, N.Q. Ren, *J. Power Sources* 198 (2012) 100–104.
- [23] X.X. Shi, Y.J. Feng, X. Wang, H. Lee, J. Liu, Y.P. Qu, W.H. He, S.M.S. Kumard, N.Q. Ren, *Bioresour. Technol.* 108 (2012) 89–93.
- [24] D.A. Lowy, L.M. Tender, J.G. Zeikus, D.H. Park, D.R. Lovley, *Biosens. Bioelectron.* 21 (2006) 2058–2063.
- [25] X. Wang, Y.J. Feng, J. Liu, H. Lee, C. Li, N. Li, N.Q. Ren, *Biosens. Bioelectron.* 25 (2010) 2639–2643.
- [26] J. Liu, Y.J. Feng, X. Wang, X.X. Shi, Q. Yang, H. Lee, Z.H. Zhang, N.Q. Ren, *J. Power Sources* 196 (2011) 8409–8412.
- [27] P. Aelterman, S. Freguia, J. Keller, W. Verstraete, K. Rabaey, *Appl. Microbiol. Biotechnol.* 78 (2008) 409–418.
- [28] Y. Liu, H. Kim, R. Franklin, D.R. Bond, *Energy Environ. Sci.* 3 (2010) 1782–1788.
- [29] Y.R. He, X. Xiao, W.W. Li, G.P. Sheng, F.F. Yan, H.Q. Yu, H. Yuan, L.J. Wu, *Phys. Chem. Chem. Phys.* 14 (2012) 9966–9971.
- [30] K.P. Gong, F. Du, Z.H. Xia, M. Durstock, L.M. Dai, *Science* 323 (2009) 760–764.
- [31] J.P. Busalmen, A. Bernal, J.M. Feliu, *Langmuir* 23 (2007) 6459–6466.
- [32] K. Guo, S. Freguia, P.G. Dennis, X. Chen, B.C. Donose, J. Keller, J.J. Gooding, K. Rabaey, *Environ. Sci. Technol.* 47 (2013) 7563–7570.

Table 2

Tafel curve conversion of untreated and electrochemical oxidation treatment with different oxidation current.

	OCP (mV vs. Ag/AgCl)	i_0 (mA m ⁻²)	KA
CC	−466	4.79	1.00
CC-3	−469	5.50	1.15
CC-7	472	6.17	1.29
CC-14	473	6.76	1.41